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(54) EXPANDABLE COMPOSITIONS AND THEIR USE IN MOUNTING CATALYST SUPPORTS

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 3M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to expandable compositions useful for positioning articles in containers and particularly for positioning catalyst supports in the casings of canisters for use as components of automobile exhaust systems. In particular, this invention relates to compositions containing unexpanded vermiculite particles which are expanded in situ to position catalyst supports in the casings of canisters.

It has become recognized that catalytic devices are needed in the control of pollution by automobile exhaust effluents, (1) for oxidation of carbon monoxide and hydrocarbons, and (2) for reduction of the oxides of nitrogen. Due to the relatively high temperatures required for these reactions, the catalyst substrate must withstand high temperatures and repeated thermal shock as well as mechanical vibration. Ceramic catalyst supports are the outstanding choice for such substrates. Because high surface areas are required for heterogeneous catalysis, ceramic substrates such as described in United State Re-issue Patent No. 27,747 are desirable.

Ceramic bodies are inherently rather brittle, and have coefficients of thermal expansion differing markedly from the coefficients of thermal expansion of metals such as are used for casings. Thus, the manner of mounting of the ceramic body used as a catalyst support in the canister is vital to the success of such catalytic devices; impact and vibration contribute mechanical shock and thermal cycling contributes thermal shock. Both thermal and mechanical shock may cause considerable attrition of the ceramic catalyst support, and attrition accelerates when it has once started, the device is quickly rendered useless.

Furthermore, because engine performance effects variations in the catalytic reactions involved and the composition of the effluent from the engine affecting the life of the catalyst, it is desirable to be able to replace the catalyst body without necessarily replacing the metal housing or casing. A simple and convenient method for mounting catalyst coated substrates or supports in casings is considered very desirable.

The invention has been made with the above points in mind.

According to the present invention there is provided a pugged expandable composition comprising:

(A) solid dry materials comprising
- (i) 30 to 80% by weight of solids of unexpanded vermiculite,
- (ii) 0 to 30% by weight of solids of inorganic binder which is synthetic mica microflakes, pulped expanded vermiculite, bentonite, hectorite, saponite, kaolinite, low melting glass or any mixture thereof,
- (iii) 0 to 25% by weight of solids of fibrous inorganic filler, and
- (iv) 0 to 40% by weight of solids of filler other than fibrous inorganic filler, therebeing at least one of components (ii) and (iv) present and the components (i) to (iv) amounting to 100% and

(B) volatile liquid vehicle in an amount in the range 10 to 55% by weight based on the combined weight of (A) and (B).

Also according to the invention there is provided a method for mounting a catalyst support in a container which comprises positioning the ceramic catalyst substrate within the container, introducing an expandable composition as described above into the

cavity between the catalyst support and the inner wall of the container in a sufficient amount to substantially fill said cavity, drying the composition to remove the liquid vehicle and thereafter expanding the unexpanded vermiculite in situ.

According to a further embodiment of the invention there is provided a canister containing a catalyst for catalytic reaction of one or more components of gas comprising a casing containing a catalyst support bearing the catalyst and held within the casing in a manner to prevent movement of the catalyst support relative to the casing by an expanded composition comprising a dried and expanded composition produced from the expandable composition as described above.

The compositions of the invention are pugged, i.e. of a putty-like consistency. The expandable compositions may advantageously be utilized as a mounting material, for example, in automobile exhaust catalytic converers. In such a use, a quantity of the putty-like composition is injected into the space between a monolithic ceramic catalyst support and the inner wall of the casing. This space is preferably not excessively large as expansion of large masses of vermiculite may crush relatively fragile ceramic pieces. Injection may be by flowing or under pressure as is convenient but pressure is preferred as it assures filling the space. After drying to remove volatile vehicle from the composition, the entire canister assembly is carefully heated to expand the vermiculite. Other methods of expansion, e.g. chemical methods, will be recognized as equivalents to heating. The expanded composition holds the monolithic ceramic core in place in the canister. The resilience of the composition after expansion serves to compensate for differences in thermal expansion between the metal casing and the ceramic substrate and to dampen vibration transmitted to the fragile device by mechanical shaking. The thermal stability assures against deterioration during operation at elevated temperatures. Additionally, the expanded mounting provides a gas tight-seal to prevent by-passing of the catalyst and thermally insulates the ceramic catalyst carrier from the casing. A further advantage of expanded compositions of the invention is their insulative value which can maintain a 200 to 350° C temperature differential across a 1 cm thickness.

The expandable compositions of the invention are useful and effective in that they are simple to use and effectively solves the problems associated with thermal and mechanical shock inherent in such devices. The compositions are inexpensive and can be used to mount irregularly shaped or dimensionally varying catalyst supports. It should be noted that several catalyst supports can also be mounted simultaneously if desired. Furthermore, it is found to be superior particularly in respect to ease of application, cost and versability of use to methods heretofore used. An illustration of one previously available method is the metallic wire packing of U.S. Patent 3,692,497 which is not only more costly and difficult to apply but additionally is fully gas-permeable and thus is not of assistance in preventing gas leakage.

The unexpanded vermiculite used in the compositions of the invention is present in an amount 30 to 80% by weight of solid materials and is preferably unexfoliated vermiculite having a particle size in the range 0.1 to 2 mm.

The inorganic binder is used in the compositions of the invention in amounts of from 0 to 30% by weight of solids. The inorganic binder is synthetic mica microflakes e.g. as disclosed in United States Patent Specification No. 3,001,571, pulped expanded vermiculite which has preferably been ground to fine particle size in aqueous suspension, bentonite, hectorite, saponite, kaolinite (ball clay), low melting glass or any combination thereof.

A sufficient amount in the range 10 to 55% by weight of the total composition i.e. (A) and (B), of volatile liquid vehicle, preferably water, is used to give a workable consistency to the mass. The exact amount varied with the characteristics of the solid materials used. Preferably the amount of water used is sufficient to give a composition which is soft enough to be worked and injected but does not contain so much water that drying is difficult.

To assist in the formation of such a workable mass, a small amount, 0 to 10% by volume based on the volume of vehicle of plasticizer may be required such as glycerine, methylcellulose, corn syrup or molasses. However, many of the clays, which may be used as binders, also assist in plasticization of the mass.

Fibrous inorganic materials are incorporated as reinforcing agents in amount of 0 to 25% by weight of solids and preferably in amount of 5 to 25% by weight of solids. Suitable fibrous materials include chrysotile or amphibole asbestos, glass fibres of various compositions such as linear spun fibres, e.g. Glasswool, and blown fibres, e.g. Kaowool, refractory filaments (crystalline alumina whiskers), or metal filaments. Preferably both linear and blown fibres are used in combination. These fibrous materials enhance the integrity of the intumescent mounting material. It may be desirable to avoid the use of asbestos because of the possible health hazards associated with this material although asbestos fibres are less expensive than other fibres. Use of glass fibre materials or refractory (glassy or crystalline) filaments or whiskers provides useful reinforcement to the final composition.

Fillers other than fibrous inorganic fillers e.g. magnesia, alumina or silica may also be included in amounts of 0 to 40% by weight solids to modify the characteristics of the final mounting material, for example, to decrease

the expansion forces when the mounting material is intumesced.

The exact procedure of combining components is not critical. Generally, the unexpanded vermiculite, binder, and any plasticizer are thoroughly mixed with sufficient liquid vehicle, e.g. water, to form a putty-like mass. When fibrous material is incorporated into the composition, excess water is normally used to form a slurry and then this slurry is filtered to reduce the water content to 15 to 20% by weight. Under such conditions, the plasticizer is not incorporated initially because it would not be retained. Instead, the filter cake is pugged with water and plasticizer, if desired, to adjust the composition to give an injectable mass of the character of moulding clay or putty containing liquid vehicle in an amount of 10 to 55% by weight based on the combined weight of (A) and (B). The injectable composition is forced into the space between the frangible and rigid components, using for example, a caulking gun or it may be forced in manually. Careful heating of the assembly including the intumescent composition first dries the mass and subsequently preferably by heating to a temperature of at least 300°C more preferably 300 to 650°C expands or intumesces the vermiculite forming a thermally resistant, resilient yet sturdy and durable mounting for the system.

Characteristics, such as bond strength, mounting or expansion force, and resilence are a function of the formulation of the compostion and dimensions of the mounting used. The extent and rate of expansion of the expandable composition are dependent upon the rate of heating, restraint applied, and the composition. The higher the concentration of unexpanded vermiculite in the composition, the greater the extent of the expansion in volume percent. Likewise, the higher the rate of heating and/or the less the restraint, the greater is the volume percent expansion within, of course, certain limits normally up to about 250% by volume. It is important to realise that the force exerted during expansion of the material may be so great as to crush a ceramic substrate. Therefore, the size of the space between the ceramic substrate and the casing must be considered in selecting the components of the expandable composition. Smaller gaps should not be filled with compositions that exhibit very high expansion in volume percent when tested against no restraint.

The durability of the mounting is tested using a "hot-shake" test. The test apparatus consists of a mechanical shaker and a source of hot gases.

A cylindrical catalyst coated ceramic substrate 11.8 cm outer diameter and 7.6 cm long is mounted in a round metal casing 12.4 cm inside diameter and 8.9 cm long with steel end ring, 1.6 mm thick × 9.3 wide having an O.D. slightly less than 12.38 cm welded into the end of the canister to retain the catalyst support which is centered in the casing resting upon the end ring. The catalyst used may be any conventional catalyst such as platinum, platinum and palladium, or copper, cobalt, chromium or vanadium containing catalysts useful for oxidation, reduction or other catalytic reactions of components of off gases, exhaust gases, or reactible gases passed through the support. The expandable composition of the invention is placed in the annular space between the inner wall of the casing and the outer surface of the ceramic substrate. A second end ring is then welded to the opposite end of the canister to securely hold the ceramic substate and the composition expanded. The metal end rings contact the face of the ceramic substrate, but the inner wall of the casing is not in direct contact with the outer surface of the substrate.

The mechanical shaker is a Model 1200 VMS air piston type vibrator (Cleveland Vibarator Co.) equipped with means to hold the cantister in a horizontal (Test A) or vertical (Test B) mode. In Test B, the vibrator is suspended from a rigid frame by four 2.5 cm × 15 cm rubber straps. The unit, operated at about 4.22 kg/cm² air pressure, provides an average acceleration of about 30 g's at 55 Hz with peak acceleration as high as 100 g's. The displacement in the vibrating mode is about three millimeters.

The source of hot gases is essentially a propane-fired blow torch. It is connected to the inlet of the canister by means of flexible metal tubing. The flame is ignited using a gas mixture at standard temperature and pressure of 793 litres per hour propane and 16,400 litres per hour air. After the catalyst substrate is warmed up (about 3 minutes operation), secondary air, 8500 litres/hr. is injected into the exhaust gas stream befofe entrance to the catalyst substrate to permit oxidation of residual propane in the catalyst zone. The temperature as the gases leave the catalyst substrate is measured by a thermocouple arrangement and varies between 600 and 700°C. As soon as the temperature is about 600°C, the vibrator is started using an air pressure of about 4.22 kg/cm², A Strobotac, available from General Radio Corp., is used to observe relative motion between the canister and core. Time for failure of the mounting is the elapsed time from beginning of the vibration until the time that the core is extruded 1.5 mm out of the exit canister and ring.

The "hot-shake" test is used as a convenient extremely severe accelerated test. No data are available which equate hours on the "hot-shake" test equipment to miles of normal test driving. Tests A and B do not necessarily give identical results on identical canisters and the purposes of tests are more for com-

parison than with the expectation that the results will correlate with results in actual practice. Thus, packings of wire gauze are relatively durable because of the springiness of the wire, but they may fail from other effects.

Tests on ceramic honeycombs mounted with expanded injectable intumescent compositions in canisters indicate the mounting is very much more durable than mountings using only the dry intumescent material poured into place and expanded. Dry vermiculite mountings as described by Slidell, in United States Patent Specification No. 1,912,544 are found to deteriorate extremely rapidly, sometimes in less than 5 minutes.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

EXAMPLE 1.

Exfoliated vermiculite of average 0.8 to 1.2 mm diameter (60 g) is added to 2000 ml water in a large Waring Blendor and agitated at high speed for about 10 minutes to form a smooth dispersion. Glass fibres (5 g, available as Fiberglass from Johns Manville Co. as JM 106 and 15 g available as Kaowool, from Babcock and Wilcox) are added and thoroughly dispersed. Vermiculite ore, that is, unexfoliated vermiculite (180 g, available as No. 4 Zonolite from W. R. Grace and Co. sieved particle size from about 0.1 to 0.5 mm), bentonite (40 g, available as Bentolite H. from Georgia Kaolin Co.) and 20 ml 1% solution off Separan NP—10 (partially hydrolyzed polyacrylamide used as a flocculant, available from Dow Chemical Company) are added and thoroughly mixed. The resulting mixture is filtered on a large Buchner funnel through No. 4 filter paper. The resulting filter cake is redispersed with a sigma blade mixer, pugged, by adding a 2% aqueous methyl cellulose solution to give a plastic composition of the invention containing 50% water and 50% solids.

The plastic mass is loaded into a conventional caulking gun and injected into the annular space (about 3 mm wide) between a circular cylindrical ceramic honeycomb catalyst support and cylindrical casing having a retaining ring at one end as described above. The gap volume of 89 ml requires 55 g (dry weight) of intumescent composition to fill the annular space. A metal retaining ring is welded in place at the other end and the assembly is heated to 600°C over a two hour period. The intumescent composition expands and fills the annular space under pressure. The entire assembly is supported in a horizontal position and connected to an exhaust gas simulator using flexible connections and with vibration directed at right angles to gas flow (Test A) as described above. The system fails in 45 minutes.

A similar system is provided for comparison using a dry mixture of 0.1 to 0.5 mm vermiculite ore as above (60 g), 0.8 to 1.2 mm exfoliated vermiculite (20 g) and bentonite (20 g) as a packing material in the annular space between the ceramic honeycomb and the canister. A portion of the above mixture (58 g) is carefully packed in the annular space (89 ml) and an end ring welded to the casing. The entire assembly is heated to 600°C over a two hour period and then mounted in the exhaust gas simulator as before. Under essentially the same conditions as above, this system fails in two minutes.

Further examples are carried out using proportions as set forth in the following Table according to the above procedure. "Hot-shake" test results of as little as 35 minutes and even less show utility for many purposes particularly where vibration is not excessively severe.

The words "Kaowool" and "Saparan" are registered Trade Marks.

TABLE

Example No.	2	3	4	5	6	7	8	9	10
Solids									
Total g.	300	300	300	300	320	300	300	320	300
Unexpanded %	60	60	60	80	47	33	60	56	60
Vermiculite (a) g	180	180	180	240	150	100	180	180	180
Binder %	13.3	0	6.7	20	25	13.3	13.3	12.5	13.3
Bentonite g.	40	–	20	60	80	–	40	40	40
Ball clay g.	–	–	–	–	–	40	–	–	–
Filler %	20	26.7	20	0	25	40	20	13.3	20
Vermiculite (b) g.	60	80	60	–	80	80	60	40	60
Magnesia g.	–	–	–	–	–	40	–	–	–
Fibres Linear %	1.7	1.7	1.7	0	3	1.7	1.7	1.6	6.7
Fiberglass g.	5	5	5	–	10	5	5	5	5
Inorganic (c) g.	–	–	–	–	–	–	–	–	15
Fibres nonlinear %	5	11.7	11.7	0	0	11.7	5	18.3	0
Kaowool	15	35	35	–	–	35	15	55	–
Vehicle Solvent									
Water 1.	2	2	3	3	2	2	0.8	2.5	2
Ethanol 1.	–	–	–	–	–	–	1.2	–	–
Plasticizer									
Methyl cellulose (d) cc.	200	200	200	230	–	200	200	200	–
Glycerine	–	–	–	–	25	250	–	–	25
Flocculant									
Separan (e)	20	20	–	–	–	–	–	–	–
Hot Shake Test (min.)	390*	143	350	175	35	106	150	357	80

Notes for Table.

(a) unexpanded vermiculite approximately 0.2 to 0.5 mm except 0.2 to 0.8 mm in Ex. 4.

(b) exfoliated vermiculite

(c) an aluminium borosilicate fibre of the type disclosed in British Patent Specification No. 1387277

(d) as 2% solution

(e) as 1% solution

* not failed when test discontinued

WHAT WE CLAIM IS:—

1. A pugged expandable composition comprising:
(A) solid dry materials comprising
(i) 30 to 80% by weight of solids of unexpanded vermiculite,
(ii) 0 to 30% by weight of solids of inorganic binder which is synthetic mica microflakes, pulped expanded vermiculite, bentonite, hectorite, saponite, kaolinite, low melting glass or any mixture thereof,
(iii) 0 to 25% by weight of solids of fibrous inorganic filler, and
(iv) 0 to 40% by weight of solids of filler other than any of (i) to (iii), there being at least one of components (ii) and (iv) present and the components (i) to (iv) amounting to 100% and
(B) volatile liquid vehicle in an amount in the range 10 to 55% by weight based on the combined weight of (A) and (B).

2. A composition as claimed in Claim 1 in which the fibrous inorganic filler is present in an amount in the range 5 to 25% by weight of the solid dry materials.

3. A composition as claimed in claim 1 or claim 2 which additionally comprises from 0.5 to 10% by volume of plasticizer based on the volume of liquid vehicle.

4. A composition as claimed in any of claims 1 to 3 in which the unexpanded vermiculite is unexfoliated vermiculite having a particle size from 0.1 to 2 mm.

5. A pugged expandable composition substantially as herein described with reference to any of the Examples.

6. A method for mounting a catalyst support in a container which comprises positioning the ceramic catalyst substrate within the container, introducing an expandable composition as claimed in any preceding claim into the cavity between the catalyst support and the inner wall of the container in a sufficient amount to substantially fill said cavity, drying the composition to remove the liquid vehicle and thereafter expanding the unexpanded vermiculite in situ.

7. A method as claimed in claim 6 in which the expansion of the unexpanded vermiculite is effected by heating to a temperature of at least 300°C.

8. A method as claimed in claim 7 in which the expansion of the unexpanded vermiculite is effected by heating to a temperature in the range 300 to 650°C.

9. A method as claimed in any of claims 6 to 8 in which the catalyst support is a ceramic catalyst substrate.

10. A method for mounting a ceramic catalyst substrate in a container substantially as herein described with reference to any of the Examples.

11. A mounted catalyst when prepared by a method as claimed in any of claims 6 to 10.

12. A canister containing a catalyst for catalytic reaction of one or more components of gas comprising a casing containing a catalyst support bearing the catalyst and held within the casing in a manner to prevent movement of the catalyst support relative to the casing by an expanded composition comprising a dried and expanded composition product from the expandable composition as claimed in any of claims 1 to 5.

13. A canister as claimed in claim 12 in which the catalyst support is a ceramic catalyst substrate.

14. A canister as claimed in claim 12 substantially as herein described with reference to any of the Examples.

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